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Retrospective Monitoring of Inorganic Materials

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RETROSPECTIVE MONITORING OF INORGANIC MATERIALS

by

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The literature has been reviewed for biological samples which are datable and have been characterized for one or more inorganic chemicals. These data are evaluated with respect to their known or estimated past exposures. It is concluded that only selected repository samples and tree rings appear to fulfill the requirements for retrospective monitoring materials.

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SECTION 1

INTRODUCTION

The potential increase of metal pollutants within the local, regional, and global environments requires additional effort in monitoring all media for contaminants. The development of a chronological reference point to which these present levels can be compared is increasingly needed. Although limited information on metal levels in selected media has been published in the primary literature, the quantity, quality, and applicability of the observations are in some doubt. In particular, except for some exceptional papers, observations prior to 1955 often suffer from the lack of the availability of accurate and precise analytical methodology. Vinogradov (1954) summarized these observations prior to 1952. Advances in analytical technology during the last twenty-five years have driven the "detection limits" for most metals to the "parts per billion" level. Presently the levels of metals in most media can be accurately and precisely determined; however, the data base and background information for the chronological reference point has not been created. Thus, it becomes necessary to determine the feasibility of gathering the data to obtain or extrapolate metal levels at a chronological reference point on a retrospective basis.

Few representative articles directed toward the area of retrospective monitoring exist in the literature. There are two important publications which describe the change in heavy metal concentration as a function of time. Johnsen and Rasmussen (1977) determined Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn in epiphytic Pterogonium gracile, a bryophyte, collected over the period 1944-1976. A statistically significant increase was observed for the Pb, V, and Zn content of this bryophyte, reflecting doubling lives of 20, 60, and 110 years, respectively. Slight increases were observed for Cu, Cr, and Ni; no concentration change was observed for Cd, while Fe and Mn content decreased. The latter effect was related to the increase in the shelter effect of plants adjacent to the sampling site.

A study of the change in particulate material over the period 1957-1974 in the U.K. was performed by Salmon et al. (1978). The study was performed using a high volume air sampler in a rural area in southern England. The concentrations of 27 elements were determined. Three types of concentration variations were observed:

1. A seasonal variation which occurred primarily between the summer and winter months.

2. Medium term fluctuations which were represented as increases and/or decreases about a general level over a period of years.

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3. Long term trends for the survey period.

Seasonal variations were observed for most elements. This was characterized by an increase in the ratio of chalcophilic elements to lithophilic elements during the winter when compared to the summer season. Similar medium term fluctuations were observed for all elements except sodium. Since the major origin of sodium in this area is sea water, it was suggested by the authors that these elemental fluctuations were meteorologically dependent and that the majority of the elements have a common origin.

Numerous long term trends were observed for the elements. The chalcophilic group, Sb, As, In, Hg, Se, Ag, and Zn, were observed to decrease over the study period. This was attributed to the enactment of the 1956 "Clean Air" Act. For zinc, a change in the emission of an industrial source was cited as the probable cause. Monitoring of the lithophilic group produced inconsistent results. Four elements, Al, Cu, Fe, and Sc, decreased in concentration, while Cs, Ce, and Th showed no statistical variation. Lead and bromine, originating from transportation and industrial operations, increased markedly during the study period.

Numerous publications indicate that monitoring on a retrospective basis can be accomplished only if the following parameters can be defined:

A. The media to be sampled must be capable of retaining a pollutant for a defined period of time.

B. The media to be sampled must show a defined rate of change of metal burden with exposure.

C. The portion of the media sampled must have properties that allow dating.

D. The quantity of sample(s) must be adequate for statistical analysis.

Effective monitoring in retrospect requires that numerous variables be defined for each of the four parameters such as the type and form of sample, the type of pollutant and the time span of observation.

Three major types of samples can be considered: surface (living); internal (living); and repository samples. Surface (living) samples are those which retain pollutants collected by deposition. An example is the deposition of particulates on leaves, bark, mosses and lichens. Internal (living) samples are those in which the pollutants have been incorporated during metabolic processes of the organism. Examples are internal animal tissues and rings of trees. Repository samples include dated collections of preserved materials in museums and herbariums.

POLLUTANT RETENTION

Retention of a pollutant is dependent upon numerous metabolic and environmental factors. The effect of metabolic fluids or water on the

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leaching or exchange rate of a pollutant from the sample medium to the surrounding environment must be defined. Samples derived from any liquid environment seemingly would have been subject to high pollutant mobility. A situation of quantitative retention of a pollutant coupled with minimal diffusion would be ideal.

If the three major types of samples are considered, it becomes apparent that each is susceptible to a particular rate of pollutant loss. Surface samples for pollutant retention (deposition) are dependent upon the activity of the medium and the ambient environmental conditions to which the medium is exposed. The retention of a pollutant within internal samples (living) is dependent on the metabolic functions of the medium, and modified by many factors such as sex, age, health, species variability, environmental change, tissue/pollutant affinity, multiple pollutant synergism, and absorption efficiency. Thus, it is obvious that the use of any tissue for retrospective analysis which has incorporated the material during the life processes of ingestion, digestion, and absorption, will be accompanied by many undefined variables. The use of these samples for retrospective monitoring virtually becomes impossible.

The third type of sample, repository, can be used for deposition measurements, presuming that the effect of sample treatment is definable and/or negligible. Because of the arguments discussed previously, only the surface samples can be used for retrospective observations.

EXPOSURE/BODY BURDEN DEFINITION

The second major requirement, which is that the sample have a defined rate of change with exposure, constitutes an additional barrier to the development of accurate methods of retrospective monitoring. If the major types of samples are considered as a group, the major problem is again associated with the rate of loss during and after the exposure period.

DATABILITY

The third parameter, datability requires that the specimen be amenable to geologic, biologic or physical/chemical dating. Each dating technique has limited sample populations. Geologic dating by stratification techniques is only applicable to deep core samples which cover long time periods of thousands of years. Biological dating techniques which define the growth pattern markers of living materials are neither widely applicable nor normally accurate. These techniques use such things as tree rings, fish scales and mollusk shells which normally involve time periods of ten to one hundred years. Tree rings appear to be the most applicable means of dating over a short period of time. Physical/chemical dating techniques, such as radioactivity and thermoluminescence, are used to date over long time periods. Radiocarbon techniques have been widely applied, while thermoluminescence has had limited use.

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In summary the application of the above techniques for exact dating covering short periods of time (≈50 years) is doubtful. Few techniques are available which can be applied to retrospective monitoring in the recent past. However most techniques may have some usefulness for dating samples prior to the industrial revolution.

Repository samples are dated at the time of collection and do not require further dating.

SAMPLE AVAILABILITY

Availability of adequate samples when included with the previous three criteria, limits the overall possibility for retrospective monitoring. Both quantity and quality of samples must be sufficient to establish statistical validity of the data. Accessibility of repository materials as well as numbers of samples and geographic coverage may be assumed to be limited.

A series of possible matrices which might be used for retrospective monitoring on a limited basis will be discussed. A list of media is given in Table 1, but excludes certain types of samples, such as ice, because of the obvious lack of adherence to the four previously discussed criteria. This list was taken primarily from sample media which are used as indicators for present or future environmental contaminations. Not all species presently used are discussed because of the differential criteria associated with present indicators and retrospective monitors. For indicators of current pollutant levels the criteria as listed below are fewer and less restrictive:

1. The number of samples must be sufficient to statistically generate data.

2. The sample must have an exposure/burden relationship. A known rate of change with exposure is necessary; however, samples obtained from pristine areas must be available for reference.

Dating of the sample is not necessary since observations are made in the present time period. Also sample availability is much less a problem than when retrospective observations are desired.

TABLE 1. POSSIBLE SAMPLE MEDIA FOR RETROSPECTIVE MONITORING

Algae and Fungi	Keratinized Materials
Bryophytes (Mosses) and Lichens	Feathers
Tree rings	Hair
Other Plant Materials	Nails
Mollusk shells	Repository Samples
Fish	Herbarium
Bones and Teeth	High Volume Repository
	Museum

SECTION 2

CONCLUSION

When the criteria of pollutant retention, exposure/burden definition, datability and availability of samples are considered, it is evident that only selected repository samples fulfill these requirements. Herbarium samples and filter mats from high volume air samplers appear to be the most promising types of samples. These are, however, limited by availability. Retrospective monitoring is possible only for those materials and in those areas where adequate samples already exist.

SECTION 3

RECOMMENDATIONS

The major problem which is presently associated with the applications of retrospective monitoring is the lack of datable material having a defined metal exposure/burden relationship. Thus, to pursue retrospective monitoring, it is recommended that sample repositories be established to be used solely for retrospective monitoring at some future time. The following conditions must be considered:

1. Determine which materials would be most suitable for environmental monitors.

2. Determine the specific collectors of specific pollutants.

3. Standardize the techniques to preserve samples.

4. Select the sampling sites.

Additional basic knowledge with respect to long term exposure and species adaptation is needed and also the development of predictive systems for toxic chemicals.

SECTION 4

DISCUSSION

ALGAE AND FUNGI

Phillips (1977) suggested that the macroalgae and bivalve mollusks are the "most efficient and reliable (biological) indicators developed to the present time" for marine and estuarine environments. Their normal physiology as well as the many variables affecting their metal uptake have been carefully studied and they are widely distributed. The algae reflect the "soluble trace metal content of their ambient surroundings" rather than the metal associated with organic or inorganic particulate matter. The bivalves, which are filter feeders, derive trace metals from their food and solution as well as from ingested inorganic particulate matter. Some of the variables affecting trace metal accumulation are species differences, seasonal fluctuations, position of sample in relation to the shoreline, salinity, temperature and relative concentrations of ions in the water. Phillips suggested that the use of both macroalgae and bivalves might be most beneficial in assessing metal loads in marine and estuarine environments.

A fresh-water filamentous alga, Cladophora glomerata was used as a biological monitor for trace metals by Keeney (1976). He identified variables similar to those described by Phillips but concluded that this organism would be a suitable bioindicator.

Presently these types of algae have a low potential as retrospective monitoring organisms since they are generally preserved in liquid and therefore subject to leaching of the elements to be tested. If appropriate preservation techniques can be developed, the algae have potential as monitoring organisms of heavy metals for future comparisons.

Higher fungi have been analyzed for trace elements. Byrne (1976) determined 10 elements in 27 species. The elements were As, Br, Cd, Cu, Hg, I, Mn, Se, Zn, and V. Soils from the collection sites were analyzed also. The levels of the 10 trace elements were generally considerably higher in the fungi than in other land plants and accumulation of mercury and cadmium was marked. Several species of basidiomycetes were found to accumulate specific elements: 1) Amanita, bromine, 2) Boletus, selenium, and 3) Lycoperdon perlatum, a puffball mushroom, arsenic, copper, mercury, selenium, and zinc. Again, usefulness for retrospective observations would depend on herbarium specimens being available in adequate numbers and also on the determination of the best species for measurement of a particular contaminant.

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A number of other plant materials have been used as biological monitors. Several show promise as retrospective monitors provided adequate numbers are available in museum collections.

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LICHENS AND MOSSES

Lichens and mosses are plants without roots or vascular systems. Consequently their supply of mineral elements depends largely on uptake from atmospheric sources. A lichen is composed of two different organisms: a fungus and an alga. Essentially they are fungi united with algae having a common method of nutrition. Lichens are a very successful group of symbiotic organisms exploiting a wide range of habitats throughout the world. Over 18,000 species have been identified. Lichens have a slow and variable growth rate. Plants which are several centuries old are found in Britain (Hawksworth, 1976). In most cases the life span of a lichen is a function of the longevity of its host and competition with other plants. Mosses, a class of Bryophytes, are distinguished by the absence of a vascular system, and do not have true roots, stems or leaves. They are small land plants which are generally found in moist environments.

Lichens and mosses are considered as indicators primarily because they are effective in adsorbing (or absorbing) airborn particulates and materials dissolved or suspended in the aqueous solutions to which they are exposed.

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Numerous articles are available which describe concentrations of metals in lichens in relation to atmospheric deposition, pH, species, mineralized substratem and mechanisms of uptake and release. Nieboer et al. (1978) reviewed the recent available data on elemental levels in lichens and discussed the various established and proposed mechanisms of mineral accumulation and release in these organisms. Table 2 presents a survey of characteristic mineral levels in lichens. They emphasized that the mineral content of even a single species was a function of the nature of the substratum and the ecosystem in which the sample existed. Moreover the authors stated that the mechanism of uptake and release of metal ions in lichens consisted of 1) extracellular electrolytic sorption, 2) solubilization of trapped particulate, 3) hydrolysis, 4) intracellular uptake and release, and 5) rewetting and resaturation respiration. The cellular uptake of selected metal ions is summarized in Table 3. The authors revised the mean biological residence or turnover times of Pb, Cu, Cs, Sr, and Fe. The metal turnover times were reported to be relatively short, ranging from 4 to 6.1 years, when compared to the longevity of lichens.

Anderson et al. (1978) presented a linear correlation between bulk precipitation of Cu, Pb, Cd, An, Ni, V, Cr, and Re and the concentration of those metals in lichens and bryophytes in the Copenhagen region. Table 4 shows the regional variation where Zone A is the center of Copenhagen, Zone B is the suburban area, and Zone C is the rural area. They concluded that the variation in heavy metal levels in lichens and bryophytes reflected the variation in metal deposition and that these organisms made it possible to describe in detail patterns of atmospheric heavy metal deposition.

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TABLE 2. CHARACTERISTIC LEVELS OF SELECTED ELEMENTS IN LICHENS

Element	Background Concentrations: Contents µg/gm dry wt.	Enhanced Concentrations: Contents µg/gm dry wt.	Enhanced Concentrations: Habitat or Source of Element
N	6,000-50,000		
Na	50-1,000	1,000-6,000	seashore
Mg	100-1,000	1,000-12,000	seashore
Al	300-400	1,300-1,900	coal mine tailings
P	200-2,000		
S	120-1,000(Arctic) 50-2,000	2,000-13,000	urban/industrial
K	500-5,000	5,000-9,500	seashore: fertilizer factory
Ca	200-40,000	40,000-55,000	seashore
Ti	6-150	150-3,800	urban/industrial
V	0-10	10-300	urban/industrial
Cr	0-10	25-130	urban/industrial
Mn	10-130	300-350 350-5,000	seashore urban/industrial
Fe	50-1,600	400-16,000 2,000-30,000 1,600-5,000 14,000-90,000	old slag hills seashore Fe/Cu/Ni smelter urban/industrial
Ni	0-5	10-120	seashore
Cu	1-50	15-1,100 15-250 50-200	old slag hills Fe/Cu/Ni smelter mineralized substratum
Zn	20-500	1,000-13,000 2,000-25,000	galvanized fence drippings Zn Cd smelter
Sr	0-700		
Mo	0-3	1-10	coal mine tailings
Cd	1-30	30-330	Zn Cd smelter
Hg	0-1		
Pb	3-5(Arctic) 20-100 (rural areas of Canada)	100-12,000	urban/industrial mine spoils

TABLE 3. CELLULAR UPTAKE OF SELECTED METAL IONS BASED ON K-ELUTION PATTERNS AND MOLAR EXCHANGE RATIOS

Metal Ion	Type of Uptake[a]		Experimental Evidence
	Extracellular	Intracellular	
K^+	+	+	90% of total K^+-content released after heat killing
Tl^+	+	+	molar exchange ratios: $Tl^+/Sr^{2+} \geq 4$ and $Sr^{2+}/Tl^+ = 2$
Sr^{2+}	+	-	little K^+-release in $\leq 10^{-2}$M $SrCl_2$ with significant Sr^{2+} uptake
H^+	+	-	little K^+-release in $\leq 10^{-2}$ M HCl (90% in 1 M HCl)
Ni^{2+}, Pb^{2+}, Co^{2+}, Cd^+	+	-	little K^+-release until external metal-ion concentration reached 0.2-2M
Cu^{2+}, Hg^{2+}, Ag^+	+	+	significant K^+-release at all experimental external metal-ion concentrations ($\leq 2 \times 10^{-4}$ M)

[a]Intracellular uptake is empirically defined as the ability of a moderately dilute solution ($\leq 10^{-2}$ M) to effect significant K^+ release; accumulation by dead lichen material and/or significant uptake from dilute solutions without K^+-release are accepted as indicating extracellular uptake; +, affirmative; -, negative.

Concentrations of Fe, Cu, Zn, Pb, Ni, and Cd were measured in nine moss and lichen species from 57 sites in coniferous woodland surrounding a brass foundry in Sweden (Folkeson, 1978). The purpose of this study was to calibrate metal levels in species not found in an area with those in species indigenous to that area. Calibration factors for estimating metal concentrations in Hylocomium splendens are presented in Table 5. This technique appears to be applicable to current monitoring of areas. However, the calibration factors varied with a change in particulate size, pH of the water in contact with the lichen or moss, and differences in growth rates between and within species.

TABLE 4. HEAVY METAL DEPOSITION ON COPENHAGEN AREA

[Heavy metal concentrations in bulk precipitation, BP ($mg \cdot m^{-2} \cdot yr^{-1}$), epiphytic lichens (ppm dry weight), epigeic bryophytes (ppm dry weight), and top soil (ppm dry weight) in the Copenhagen areas (mean ± SD)]

Metal		Zone C	Zone B	Zone A
Cu	BP	3.3 ± 0.8	6.2 ± 1.4	12.3 ± 3.9
	Lichens			
	Bryophytes	23 ± 12	32 ± 28	48 ± 25
	Soil	6.5 ± 2.8	9.8 ± 5.0	46 ± 23
Pb	BP	22 ± 7	48 ± 18	80 ± 24
	Lichens	76 ± 31	109 ± 76	232 ± 80
	Bryophytes	92 ± 54	91 ± 42	132 ± 43
	Soil	24 ± 5	43 ± 14	116 ± 40
Cd	BP			
	Lichens	0.34 ± 0.59	0.89 ± 1.14	0.75 ± 0.38
	Bryophytes	0.49 ± 0.19	0.52 ± 0.28	0.77 ± 0.36
	Soil			
Zn	BP	41 ± 14	88 ± 20	118 ± 23
	Lichens	85 ± 12	85 ± 11	109 ± 35
	Bryophytes	147 ± 69	173 ± 130	245 ± 109
	Soil	36 ± 12	50 ± 22	244 ± 175
Ni	BP	1.5 ± 0.1	2.8 ± 0.8	3.8 ± 0.9
	Lichens			
	Bryophytes	8.9 ± 3.8	12.5 ± 6.4	16.3 ± 6.5
	Soil			
V	BP	3.7 ± 0.7	6.9 ± 2.1	10.5 ± 3.8
	Lichens	19	12 ± 1	14 ± 3
	Bryophytes	11 ± 5	13 ± 7	19 ± 9
	Soil			
Cr	BP			
	Lichens			
	Bryophytes	5.6 ± 4.5	6.3 ± 2.7	15.6 ± 18.0
	Soil	8.0 ± 2.7	7.3 ± 1.5	85 ± 130
Fe	BP	155 ± 46	290 ± 99	549 ± 194
	Lichens			
	Bryophytes	2,590 ± 1,440	3,530 ± 2,020	3,870 ± 1,710
	Soil	6,100 ± 1,600	6,300 ± 1,200	9,700 ± 2,500

TABLE 5. CALIBRATION FACTORS (MEAN ± 95% CONFIDENCE LIMITS) FOR ESTIMATING METAL CONCENTRATIONS IN HYLOCOMIUM SPLENDENS FROM CONCENTRATIONS MEASURED IN ANY OF THE OTHER EIGHT SPECIES

	Fe	Cu	Zn	Pb	Ni	Cd
Dicranium polysetum	1.14 ± 0.16	1.25 ± 0.28	0.90 ± 0.14	1.46 ± 0.17	1.60 ± 0.22	1.5 ± 0.2
Hypnum cupressiforme	0.39 ± 0.06	1.11 ± 0.27	0.78 ± 0.13	0.44 ± 0.06	0.68 ± 0.09	0.9 ± 0.1
Pleurozium schreberi	1.11 ± 0.19	1.37 ± 0.28	0.97 ± 0.14	1.31 ± 0.18	1.70 ± 0.23	1.7 ± 0.3
Pohlia nutans	0.52 ± 0.09	1.00 ± 0.30	0.68 ± 0.12	0.68 ± 0.10	0.94 ± 0.10	0.7 ± 0.1
Cladonia rangiferina	1.49 ± 0.26	2.81 ± 0.74	1.59 ± 0.28	2.04 ± 0.27	3.20 ± 0.41	2.7 ± 0.5
Hypogymnia physodes	0.78 ± 0.11	1.43 ± 0.35	0.70 ± 0.12	2.05 ± 0.24	1.80 ± 0.18	1.2 ± 0.2
Pseudevernia furfuracea	0.71 ± 0.10	1.14 ± 0.24	0.68 ± 0.12	1.24 ± 0.15	1.70 ± 0.17	2.2 ± 0.3
Usnea filipendula	1.08 ± 0.20	1.79 ± 0.40	0.89 ± 0.16	1.72 ± 0.20	1.80 ± 0.26	2.2 ± 0.3

Rühling and Tyler (1969) determined regional and historical changes of selected metals in moss collected in Skåne, Sweden. The authors reported an increase in Cu, Zn, Ni, and Cr concentrations in Hypnum cupressiforme, collected from 1870-1969 (Table 6). They concluded that the increase in concentration of these metals was a result of an increase in industrial activity.

Rasmussen (1977) in a study in Denmark reported a significant increase in metal concentrations in bryophytes during the last 25 years. Herbarium material collected in 1951 was compared with recent collections from the same trees. It was concluded that in rural areas the Cr, Cu, Fe, Ni, Pb, V, and Zn concentrations in epiphytic bryophytes which increased during this time coincided with the rapid increase in the combustion of fossil fuels.

. . . .

Rasmussen and Johnsen (1975) made relative comparisons of Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, S, V, and Zn concentrations of an epiphytic moss to bulk precipitation and to concentrations in phorophyte bark. Their data are presented in Table 7. They concluded that most of the elements which accumulated in the moss originated from the atmosphere.

Measurement of metal concentrations in bryophytes has been used to study regional distributions of heavy metal pollution in areas of Finland, (Pakarinen and Tolonen, 1976, 1977); New Zealand, (Ward et al. 1977); northwestern Ontario, Canada, (Barclay-Estrup and Tinne, 1978); Scandinavia, (Rühling and Tyler, 1973); and northeastern United States, (Broet, 1976). The results indicate a positive correlation between metal concentrations in mosses and industrial activity.

From the literature the following conclusions can be made:

1. Mosses and lichens are capable of retaining some metals for a defined period of time.

2. Herbarium collections allow dating at selected sites.

3. A statistical sample size exists for analysis.

If more information were available concerning the change of pollutant concentrations in lichens and mosses as a function of pH, particulate size, wind velocity, moisture and growth rate, then these organisms would appear to be acceptable materials for retrospective monitoring of atmospheric metal concentrations.

TREE RINGS

Many authors have suggested that trees would be suitable organisms for retrospective monitoring since they represent a datable long-lived biological system. Furthermore a statistical sample size is available for analysis.

TABLE 6. STATISTICAL CALCULATIONS ON THE HISTORICAL CHANGES. MEANS (PPM) AND SIGNIFICANCE OF THE DIFFERENCES BETWEEN THE MEANS

	Means (ppm)				t-Values and Levels of Significance			
	1870/99	1900/19	1920/43	1969	1870/99-1900/19	1900/19-1920/43	1920/43-1969	1870/99-1969
Cu	10.2	13.0	13.5	13.9	1.73	0.30	0.30	2.74*
Zn	66.0	94.0	103.0	109.0	2.23*	0.70	0.71	5.49‡
Ni	4.0	3.7	5.5	9.1	0.55	4.12†	10.20‡	10.70‡
Cr	5.8	5.5	6.5	7.7	0.27	1.15	1.36	1.74

Level of significance: * = $p < 0.05$
† = $p < 0.01$
‡ = $p < 0.001$

TABLE 7. CONCENTRATIONS (PPM DRY WEIGHT) OF CHEMICAL ELEMENTS IN BULK PRECIPITATIONS, EPIPHYTIC MOSS, AND PHOROPHYTE BARK
(Standard deviations in parenthesis.)

Element	Phorophyte	Precipitation		Moss		Bark	
Ca	Fraxinus	1.7	(0.2)	4,000	(2,000)	17,000	(4,000)
	Fagus			2,000	(1,000)	18,000	(9,000)
Cd	Fraxinus	0.001	(0.00005)	0.35	(0.04)	0.08	(0.04)
	Fagus			0.44	(0.15)	0.25	(0.07)
Cr	Fraxinus	0.004	(0.001)	2.6	(0.8)	3.8	(0.7)
	Fagus			3.4	(1.4)	2.6	(0.7)
Cu	Fraxinus	0.02	(0.01)	12	(3)	16	(1)
	Fagus			8	(4)	21	(5)
Fe	Fraxinus	0.30	(0.10)	2,000	(400)	1,100	(100)
	Fagus			2,500	(700)	600	(200)
K	Fraxinus	2	(1)	5,000	(2,000)	3,000	(1,000)
	Fagus			5,000	(2,000)	2,000	(1,000)
Mg	Fraxinus	0.5	(0.2)	1,600	(300)	1,000	(200)
	Fagus			1,700	(700)	1,100	(800)
Mn	Fraxinus	0.03	(0.01)	120	(40)	3	(1)
	Fagus			210	(80)	32	(11)
Na	Fraxinus	3	(1)	800	(200)	1,100	(400)
	Fagus			600	(300)	300	(100)
Pb	Fraxinus	0.03	(0.01)	40	(25)	9	(3)
	Fagus			60	(22)	6	(4)
S	Fraxinus	2.5		1,600	(100)	1,700	(300)
	Fagus			1,800	(400)	900	(400)
V	Fraxinue	0.05		7	(2)	14	(9)
	Fagus			8	(4)	12	(9)
Zn	Fraxinus	0.24	(0.09)	90	(20)	60	(10)
	Fagus			100	(40)	110	(30)

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Elements such as Pb, Cr, Zn, Hg, Cu, Ag, Rb, Co, Fe, Cd, etc. have been determined in the tree rings of numerous species of trees. Considerable research has been directed toward analysis of lead in trees occupying sites close to highways and urban areas. Kardell and Larsson (1978) determined lead and cadmium concentrations in tree rings of oak. The oldest tree used in this study was 150 years old. Their results, presented in Figures 1a - 1e, are plots of concentrations versus time and clearly indicate a positive correlation between lead uptake and traffic volume, and a negative correlation between xylem lead concentrations and distance from the road.

Barnes, Hamadah and Ottaway (1976) determined lead, copper and zinc concentrations in Norway spruce and white beam from a forest site, and a city site. Their results are presented in Tables 8 and 9. They also indicated that similar results were obtained for other tree species at various locations in these two sites. The authors concluded that there was little correlation of sample site or age of the rings with airborne lead concentrations, and that rings cannot be used to identify the annual level of lead or other heavy metal pollutants.

Sheppard and Funk (1975) reported in a preliminary study that long-lived trees growing in intimate contact with rivers may be used to monitor variations of metal ion concentrations in the rivers. As shown in Figure 2, they observed a correlation of seven metals in trees and lake sediment with mining activity of the Coeur D'Alene mine in Idaho.

Tian and Lepp (1977) determined Pb and Zn concentrations in larch and sycamore. Their results, presented in Table 10, indicated that the levels of heavy metals found in annual growth rings of trees are not a function of a single variable such as the metal concentration in soil. They concluded that tree growth patterns may influence metal accumulation and the growth patterns may vary in the same species at the same site.

The ease of determining the age of trees by tree ring dating and the accessibility of statistical sample size make trees an attractive biological organism for retrospective monitoring. However, the lack of information concerning turnover times of metals in trees, the limited information concerning the transport of heavy metals in the xylem tissue, and the variability of metal concentrations with respect to growth patterns indicate that trees would not presently be a primary candidate for retrospective monitoring.

PLANT MATERIALS

In addition to those plant materials already discussed, many other plants and plant parts have been investigated as potential monitors of heavy metal contaminations of the environment. Both airborne contaminants and those derived from the soil or water in which the plants grow have been studied.

Underwood (1977) lists four basic interdependent factors which affect trace element levels in plants. These are: 1) genus, species or strain of plant (genetic differences in uptake and metabolism); 2) type of soil on

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Figure 1a. Lead concentration (ppm dw) in the xylem 1826-1975. Oak No. 2, distance from road 0.5 m. Samples were taken from the side of the tree facing the road.

Figure 1b. Lead concentration (ppm dw) in the xylem of two oaks exposed to different traffic densities. Oak No. 1 is located 19 m from a highway (40,000 vehicles/day) while Oak No. 3 grows 0.5 m from a road with low traffic volume (800 vehicles/day).

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Figure 1c. Lead concentration (ppm dw) in the xylem of two oaks growing at different distances from the road (Oak No. 2, 0.5 m and Oak No. 7, 39 m).

Figure 1d. Cadmium concentration (ppb dw) in the xylem of Oak No. 7 growing near the gasworks in Stockholm.

Figure 1e. Lead concentration in xylem of Oak No. 1 compared to the traffic density of the nearby road, during the years 1925-75. Traffic counts are done one weekday in October each year.

TABLE 8. CONCENTRATIONS OF LEAD IN TREE RINGS FROM FOREST AND CITY SITES

Tree Species	Tree Location	µg Lead/g Sample Dry Weight			
		1936-41	1942-47	1948-53	1954-59
Norway spruce	Loch Ard Forest	7	8	4	2
White beam	Glasgow Green Park	4	4.5	2	1.5

TABLE 9. CONCENTRATION OF LEAD, ZINC, AND COPPER AT FOREST AND CITY SITES

Metal	Sample	Conc. of Metal µg/g Sample Dry Weight			
		Norway Spruce Loch Ard Forest		Poplar Lombardy Botanic Gardens	
		Conc.	Bark Rings	Conc.	Bark Rings
Zinc	bark	38	2.5	60	2.3
Zinc	tree rings	15		26	
Copper	bark	5	8.3	24	16.0
Copper	tree rings	0.6		1.5	
Lead	bark	4	0.8	300	120
Lead	tree rings	5		2.5	

which the plant is grown (basic mineral content, acidity, drainage, and other factors affect mineral uptake); 3) climatic or seasonal conditions during growth; and 4) stage of maturity of the plant. Accumulator plants were identified for Se, Sr, Al, As, and Co.

It is apparent that for any study baseline data is needed to determine the mineral patterns of the soil profile and specific plant. Pietz et al. (1978) did such a study on corn grains from nine different areas of Illinois.

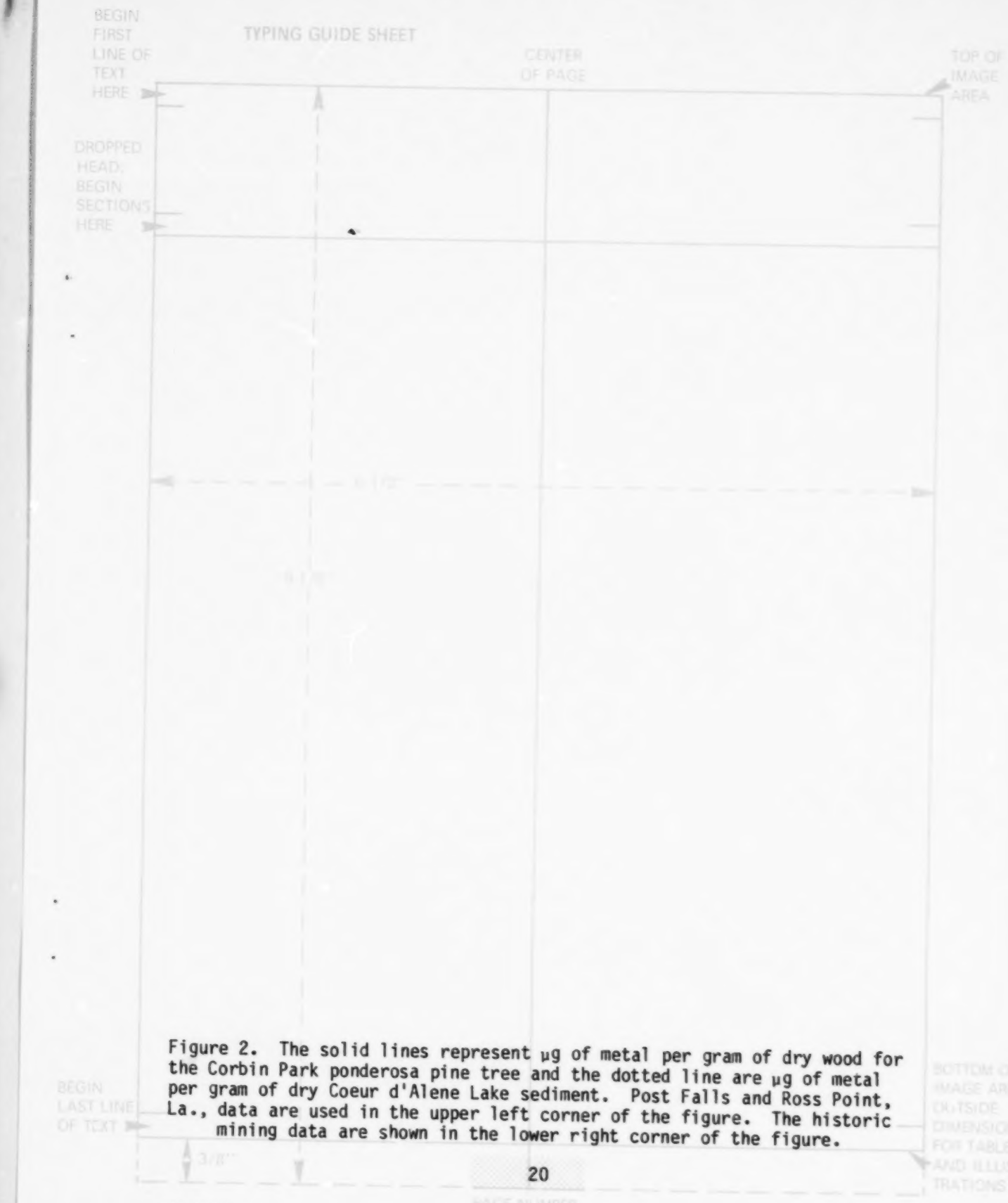

Figure 2. The solid lines represent µg of metal per gram of dry wood for the Corbin Park ponderosa pine tree and the dotted line are µg of metal per gram of dry Coeur d'Alene Lake sediment. Post Falls and Ross Point, La., data are used in the upper left corner of the figure. The historic mining data are shown in the lower right corner of the figure.

TABLE 10. LEAD AND ZINC CONTENTS OF ANNUAL GROWTH RINGS OF EUROPEAN SYCAMORE (ACER PSEUDOPLATANUS) AND EUROPEAN LARCH (LARIX DECIDUA) GROWING ON SOILS WITH ABOVE NORMAL LEAD AND ZINC CONTENT

HALKYN - LARCH

a) Soil Conditions

pH	Pb	Zn
4.8 ± 1.1	47.1 ± 4.5	182.4 ± 14.9

b) Tree Core Analysis

Chronological Wood Age (yr)	Ring Weight	Pb Cont.	Zn Cont.
0 - 10	0.165 ± 0.009	6.99 ± 1.61	17.9 ± 4.5
11 - 20	0.174 ± 0.012	7.49 ± 2.18	12.2 ± 4.0
21 - 30	0.227 ± 0.019	3.15 ± 2.14	14.2 ± 5.7
31 - 40	0.294 ± 0.027	1.99 ± 0.64	10.4 ± 6.1

LONG RAKE - SYCAMORE

a) Soil Conditions

pH	Pb	Zn
4.2 ± 1.0	16.8 ± 3.2	59.8 ± 6.2

b) Tree Core Analysis

Chronological Wood Age (yr)	Ring Weight	Pb Cont.	Zn Cont.
0 - 10	0.155 ± 0.053	57.6 ± 10.4	24.1 ± 3.2
11 - 20	0.140 ± 0.015	17.6 ± 4.9	12.7 ± 2.1
21 - 30	0.180 ± 0.021	23.5 ± 7.2	14.2 ± 2.4
31 - 40	0.223 ± 0.041	35.9 ± 9.5	14.1 ± 2.4
41 - 50	0.402 ± 0.095	81.1 ± 26.2	17.7 ± 3.8

Larch data based on 8 replicates, Sycamore data on 9 replicates for each age-group. Ring weight expressed in g, Pb and Zn levels as µg element/g dry weight wood. All results given ± S.E. Soil metal levels are acetic-extractable, given as µg/metal/g air dry weight soil.

Twelve elements as shown in Table 11 were studied and significant variations were found in grains from the various locations.

Changes in plant mineral content in response to additions of various kinds to the soil have been and are being extensively studied. Sewage sludge used as fertilizer (Ham, 1978), insecticides such as lead or calcium arsenate (Elfving, 1978), copper/chrome/arsenic wood preservative (Grant, 1977), minespoil (Pinkerton, 1977), metal smelter emissions (Buchauer, 1973, Jackson, 1978), and vehicle exhaust (Motto, 1970) have all been examined in relation to heavy metal increases in plant tissues. Clear evidence of species differences in metal uptake and metabolism was shown in the copper/chrome/ arsenic preservative experiments in which pot-grown crops of carrots, green beans and tomatoes were tested. The three minerals in the carrots were correlated with the soil levels. The tomatoes showed a correlation with soil levels for chromium and arsenic, whereas the metal content of the bean crop did not correlate with the soil levels of the three elements.

Both mercury (Beauford, 1977) and lead (Malone, 1973 and Zimdahl, 1978) were shown to accumulate in the roots in much greater quantities than the other plant tissues.

An interesting study with respect to species differences was done with nine varieties of lettuce grown hydroponically at six substrate levels of concentration of Pb. The results showed varietal differences in top and root tissue Pb concentrations, amounts assimilated and translocation to edible tissue, as well as differences due to substrate lead concentration and deviation of exposure (John, 1977).

All the studies of plants or plant materials used as biological monitors of heavy metals emphasized that specific monitors for specific substances must be chosen. Thus a great deal of background information on metabolism and on baseline levels and patterns for any given location and species must be obtained before any valid comparisons can be made.

Criteria proposed by Ray and White (1979) for plants which might be used as biological monitors for heavy metals are:

1. Species must be representative of the area.
2. Species must be widely distributed and easy to collect.
3. Species must have a high tolerance for heavy metals and a high concentration factor.
4. Species must be readily identifiable.

For use in retrospective monitoring, the additional requirements of datability and defined rate of accumulation with exposure must be satisfied.

TABLE 11. ELEMENTAL ANALYSES OF CORN GRAIN FROM ILLINOIS ARGRONOMY RESEARCH FIELDS AND FULTON COUNTY (µg/g*)

Location	Corn Grain Elements†											
	Ca	Fe	K	Mg	Mn	Na	Cd	Cr	Cu	Ni	Pb	Zn
Research fields												
Aledo(n=20)	40.3c	27.4d	3,400d	1,090d	5.61e	10.2c	0.055e	0.094c	2.69e	0.91d	0.191cd	16.4ab
Brownstown(n=36)	65.1g	19.6ab	2,900b	1,080cd	6.12g	6.1a	0.080f	0.110d	2.68e	0.78c	0.170bc	18.8c
Carthage(n=20)	25.8a	17.9a	3,680e	1,020b	5.63e	6.6a	0.010a	0.059a	2.60de	0.49a	0.192cd	20.1d
DeKalb(n=192)	57.3f	19.6a	2,990b	1,070c	5.40d	6.6a	0.037c	0.073b	2.18b	0.79c	0.141a	20.7e
Dixon(n=20)	33.7b	18.8a	2,940b	954a	4.92a	7.2a	0.034c	0.068ab	2.49d	0.78c	0.149ab	16.9b
Elwood(n=60)	53.3e	21.4bc	2,820a	1,100d	5.83f	8.4b	0.026b	0.118d	3.22f	1.43f	0.133a	19.0c
Hartsburg(n=36)	33.9b	19.3a	3,230c	1,150e	5.06b	10.5c	0.051e	0.094c	1.67a	1.03e	0.213d	17.1b
Kewanee(n=20)	44.5d	22.8c	3,120b	963a	5.30c	15.1d	0.046d	0.193e	4.41g	0.58b	0.184c	15.7a
Urbana(n=24)	40.0c	20.7bc	3,440d	1,085d	5.78f	9.8c	0.012a	0.059a	2.29c	0.80	0.243e	18.6c
Fulton County												
Clinton-Hickory-Keomah(n=6)	39.9a	19.2a	3,490c	1,000a	6.34b	5.9b	0.043c	0.107d	2.73a	0.83c	0.204a	21.4a
Fayettee-Hickory-Rozetta(n=6)	46.4b	23.0c	3,370b	1,180bc	6.28b	7.4c	0.032c	0.078c	3.95b	0.80c	0.226a	24.3b
Ipava-Sable(n=6)	41.3a	20.7b	2,860a	990a	4.58a	6.5bc	0.042cd	0.099cd	2.82a	0.80c	0.230a	21.7ab
Lawson-Titus-Beaucoup(n=6)	37.9a	21.4bc	3,450c	1,150bc	5.05a	7.8c	0.053d	0.078c	3.76d	0.80c	0.204a	21.6ab
Tama-Ipawa(n=6)	35.6a	21.4bc	3,280b	1,090ab	6.56bc	4.2a	0.015a	0.047a	3.64b	0.62a	0.180a	22.5ab
Mine-Spoil(n=28)	47.0c	20.6b	3,410c	1,210c	6.91c	7.4c	0.023b	0.065b	3.76b	0.73b	0.230a	22.0ab

*Means in each vertical column of research fields and Fulton County, respectively, followed by the same letters are not significantly different at the 5% level using Student-Newman-Keul's Test modified for unequally replicated treatments.
†Populations represent duplicate analysis of field samples.

MOLLUSKS

Mollusks have received considerable attention as potential retrospective monitoring organisms. Metal concentrations of Pb, Cd, Zn, Cu, Ag, Co, Ce, Fe, Mn, Hg, and Ni have been determined in shells.

Anderson (1977) determined concentrations of Cd, Cu, Pb, and Zn in six species of clams collected in the Fox River in Illinois and Wisconsin. He observed, as presented in Table 12, that tissue concentrations of metals were higher than shell concentrations. The order of metal concentrations in the shells was Cd<Cu<Zn<Pb.

Coughtrey and Martin (1977) studied the concentrations of Pb, Zn, Cd, and Cu in Helix aspersa collected from two different sites of varying degrees of metal contaminations. It was concluded that because of a positive linear relationship between metal uptake and body weight, mollusks of similar weight and/or size should be used for monitoring purposes. The different patterns of metal uptake by different organs require a comprehensive study of the physiological aspects of heavy metal uptake in mollusks.

Frazier (1975, 1976) investigated the dynamics of metal accumulation in the American oyster with respect to seasonal and environmental effects. In the seasonal effects study, he observed the following patterns of metal dynamics:

1. Mn and Fe concentrations in soft tissues correlated with shell deposition.

2. Zn and Cu concentrations were not correlated with shell growth. The Zn and Cu concentrations in the body gradually increased during the spring and early summer, followed by a rapid loss during August and September.

Frazier (1976) also observed in the environmental effects study that Zn and Cu accumulated in soft tissues of oysters exposed to high levels of these elements. The incorporation of trace metals into the shell was suppressed for Mn and slightly increased for Fe, Zn, and Cu. The uptake of metals by the soft tissues of oysters was dependent on the season where the uptake was rapid in summer and fall and delayed in early spring.

Mollusks are attractive biological organisms for retrospective monitoring because of the ability to date the shell by the growth rings, their relatively stationary geographical location, and the slow turnover rate of the metal when incorporated or trapped in the carbonate crystals. However, the available information indicates mollusks would not be reliable organisms for retrospective monitoring because the physiological relationship is unclear between metal concentration in shells and soft body parts and the surrounding waters. Furthermore knowledge is limited on the seasonal growth rates of mollusks as well as the variations in the rate of uptake of metals between the species.

TABLE 12. MEAN CONCENTRATION OF METALS IN SIX SPECIES OF CLAMS COLLECTED IN THE FOX RIVER, ILLINOIS AND WISCONSIN

Taxa and Body Parts	Number of Samples	Total Dry Weight (g)	µg Metal/g Dry Weight Tissue (standard deviation) Cd	Cu	Pb	Zn
Lampsilis siliquoidea						
shell	3	4.50	3.66 (1.23)	7.18 (2.34)	20.92 (6.33)	8.33 (1.97)
body	7	9.90	5.89 (2.20)	7.41 (3.65)	23.16 (8.82)	319.85 (67.91)
Lampsilis ventricosa						
shell	2	5.64	2.69	7.01	16.34	8.22
body	1	0.30	2.71	22.35	17.64	173.45
Strophitis rugosus						
shell	2	2.03	3.36	8.40	22.66	8.05
body	2	0.71	4.36	13.52	25.61	129.72
Sphaerium sp.						
shell	1	1.26	2.85	10.90	32.96	11.68
body	1	0.33	2.49	18.90	48.17	146.52
Anodonta marginata						
shell	5	10.31	1.35 (0.09)	9.30 (3.62)	10.19 (0.55)	3.70 (0.20)
muscle	4	3.40	0.47 (0.19)	4.11 (1.23)	1.92 (0.45)	22.11 (4.67)
gills	3	8.45	4.75 (1.71)	12.89 (1.20)	17.53 (2.69)	211.10 (21.84)
viscera	4	7.46	2.19 (0.73)	7.89 (2.24)	13.81 (1.57)	223.52 (10.63)
Lasmigona complanata						
shell	2	5.64	1.24	3.36	9.15	5.10
muscle	3	2.94	0.36 (0.11)	2.75 (1.25)	5.24 (2.83)	61.71 (22.91)
gills	2	2.76	1.11	4.05	24.92	420.69
viscera	2	4.93	0.90	2.17	13.87	270.64

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BONES AND TEETH

The calcified tissues (skeletal system) have been analyzed for the amount of P, As, Zn, and Cd.

Rabinowitz, Wetherill, and Kopple (1976) studied the steady state kinetics of lead metabolism with stable lead isotope tracers in five healthy men. They developed a very simple and revealing three-compartmental model for lead metabolism. This model is present in Figure 3. The authors also described a mathematical equivalent to the model. Their results indicated a dynamic equilibrium occurred between the bone and blood where the concentration of lead in the bone followed the blood level.

LEAD METABOLISM MODEL

Figure 3. A three-compartmental model of human lead metabolism derived from tracer and balance data from five healthy men. The lead content and mean life of each pool and the rates of lead movement between pools (λ) are shown. Numerical values represent the mean values (±SD) for all subjects for whom data were available. Loss of lead from the body via pool two (λ_{20}) is from integumentary structures (hair, nails, sweat) and alimentary tract losses, such as salivary, biliary, gastric, and pancreatic secretions.

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Strehlow and Kneip (1969) analyzed over forty samples of human bone from a single skeleton to define the skeletal distribution of lead and zinc and also analyzed two hundred teeth to define the relationship of lead concentration with age. They found, as shown in Table 13, that a greater concentration of lead appeared in the long than in the short bones and the lead concentration increased with age. They also observed that the lead concentration in teeth was approximately 4 times the concentration in bone. No conclusions were drawn for zinc.

Berry and Mossman (1970) analyzed human tissues for lead concentrations in 69 post-mortem subjects. Their data indicated lead concentrations increased with an increase in length of bone and age.

Grandjean, Nielsen, and Shapiro (1979) determined the lead concentrations in bones and teeth of 105 Nubian skeletons from the period 3300 B.C. to 750 A.D. and compared these findings with those of 17 contemporary corpses. The results in Table 14 indicated that the concentration of lead increased as environmental lead increased.

Bones and teeth are possible tissues for the retrospective monitoring of lead. However, many variables such as age, exposure periods, mineral deficiencies, disease history, and turnover rates must be defined. In addition, noncontaminating preservation techniques must be available before bones and teeth can be seriously considered for retrospective monitoring of lead.

Although the majority of studies have dealt with lead, the same considerations must be applied to other metals.

FISH

The relationships of the metal concentration in fish to those of ambient water conditions have been extensively studied for a large number of fish species. Correlations of metal concentrations to different tissues, geographical location, age of fish, species of fish, etc., have been reported by Lucas et al. (1970); Zook et al. (1976); Kelley et al. (1975); Tong et al. (1974).

Ronk (1971) proposed the following concentrating pathways for metal contaminants in fish:

1. particulate ingestion of suspended material
2. adsorption of suspended material
3. ingestion of metals via pre-concentration in food materials
4. incorporation of metal ions into important physiological systems
5. uptake by ion exchange mechanisms in soft tissues

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TABLE 13. ANALYTICAL RESULTS

Sample	Ash (%)	Lead (µg/gm ash)	Zinc (µg/gm ash)
Calvaria	50.1	105	168
Calvaria	53.1	135	163
Calvaria	50.0	87	166
Mandible	46.7	121	153
Tooth, incisor	73.8	331	
Tooth, incisor	72.3	317	
Tooth, incisor	71.9	336	
Canine	72.7	254	
Vertebra	9.9	195	199
Vertegra	4.4	215	221
Vertebra	10.4	180	239
Vertebra	6.4	237	209
Vertebra	11.2	167	237
Vertebra	11.5	120	258
Rib	12.4	120	258
Rib	17.8	183	367
Radius, proximal shaftpiece	44.8	87	159
Radius, distal shaftpiece	42.1	78	119
Radius, proximal endpiece	31.5	107	153
Radius, distal endpiece	22.3	143	185
Tibia, distal shaftpiece	27.9	131	123
Tibia, distal shaftpiece	43.6	98	144
Tibia, proximal shaftpiece	44.5	111	129
Tibia, proximal shaftpiece	34.0		128
Tibia, proximal shaftpiece	29.3	92	192
Tibia, proximal endpiece	18.3	136	172
Tibia, proximal endpiece	11.6	131	186
Tibia, distal endpiece	19.5	163	134
Tibia, distal endpiece	21.5	109	195
Fibula, proximal shaftpiece	44.1	119	167
Fibula, proximal shaftpiece	43.5	131	162
Fibula, distal shaftpiece	44.0	129	148
Fibula, distal endpiece	25.2	170	224
Fibula, proximal endpiece	19.7	175	206
Femur, distal shaftpiece	23.3	77	160
Femur, distal shaftpiece	39.3	102	170
Femur, proximal shaftpiece	45.7	81	164
Femur, proximal shaftpeice	40.1	91	143
Femur, proximal endpiece	15.3	106	
Femur, proximal endpiece	15.6	131	
Femur, proximal endpiece	23.5	90	181
Femur, distal endpiece	14.1	154	
Femur, distal endpiece	15.6	125	187
Femur, distal endpiece	15.0	121	211

TABLE 14. MEDIA BONE AND TOOTH LEAD CONCENTRATIONS IN µg/g (WITH 95 PERCENT CONFIDENCE LIMITS GIVEN IN PARENTHESIS OF ADULT INDIVIDUALS FROM DIFFERENT TIME PERIODS)

Time Period	Number of Individuals	Bone Lead	Tooth Lead
A-group (3300-2900 B.C.)	9	0.6 (0.4-1.5)	0.9 (0.4-1.4)
C-group (2000-1600 B.C.)	13	1.0 (0.5-1.6)	2.1 (0.9-3.1)
Pharaonic (1650-1350 B.C.)	15	2.0 (1.4-3.0)	5.0 (2.4-7.7)
Total A.D. (1-750 A.D.)	68	1.2 (0.9-1.6)	3.2 (2.4-4.4)
Contemporary Denmark	17	5.5 (3.7-8.8)	25.7 (17.0-42.4)
Contemporary USA	6		175.0 (122.1-233.4)

6. complexation of metals with appropriate organic molecules.

The metal concentrations in fish tissues and scales are a function of:

1. physical and chemical characteristics of the metal
2. biological turnover rate
3. metalloprotein-metal exchange
4. solubility of related derivatives
5. ionic strength of ambient water
6. physiological characteristics of the tissues of a particular species.

Lucas, Edgington, and Colby (1970) determined concentrations of trace elements in fish livers from Lake Michigan, Lake Superior, and Lake Erie. The values indicated that the metal concentrations varied with species and geographic location. The results in this document indicate that the fluctuations in metal concentrations, the complexities of the physiological characteristics of fish, the lack of information concerning biological turnover rates of metals, etc. prevent the use of fish for retrospective monitoring.

The authors of the excellent review by the Smithsonian Institution (1976) on the use of museum specimens for retrospective monitoring concluded that fluctuations in metal concentrations occur in fish specimens after initial preservation and that the levels vary in different preservatives. They concluded that fluid-preserved museum fish specimens cannot be used for meaningful timescale comparison.

KERATINIZED STRUCTURES

Keratinized structures derived from the epidermis appear to hold potential as biological monitors of heavy metals. These structures are the scales and rattles of reptiles, turtle shells, feathers, beaks, bills, claws, nails, hooves, horns, and hair of birds and mammals. Keratinized material contains no nuclei and is non-living. Therefore, it represents the environment during formation, usually a short period of days or weeks. In addition the material is subject to minimal metabolic change.

Matoltsy states in Butcher (1962) "keratinization may be considered as a specific form of cell differentiation in which metabolically highly active cells pass through various cytomorphic and physiologic changes while they reach the terminal stage and become filled with a resistant and considerably insoluble horny material." The keratin is a protein produced within the cells. It has a complex quaternary molecular structure and generally contains cystine, cysteine, glutamic acid, arginine, leucine, glycine, and tyrosine plus other amino acids. It is generally composed of two components, a fibrous protein and a globular matrix protein (Spearman, 1973). The presence in the fibrous proteins of either sulfhydryl or disulfide groups (Butcher, 1962), or both, provides loci for the attachment of metal ions.

The chitinous exoskeleton of the arthropods may also be a candidate for heavy metal monitoring. Chitin is a neutral mucopolysaccharide which always occurs in nature bound to protein. It occurs in the cuticle along with fibrous sclerotin. Calcite is often deposited to add further strength and rigidity (Spearman, 1973). The exoskeleton is subject to periodic molting and would also represent a relatively short period of time. Silk which is a protein secretion of epidermally derived glands would also bear examination as a metallic ion monitor.

Carefully standardized sample preparation is required to distinguish metabolically - incorporated from surface - adsorbed metals or other pollutants.

A number of keratinized materials which have been used as biological monitors are considered in greater detail in the following sections.

Feathers

A number of studies have indicated that feathers may be useful monitors of mineral intake but subject to many variables. Molting, the period of feather growth and mineral incorporation, occurs over a very short time of 2-4 weeks. Therefore the mineral content of the feathers does not represent the

life of the bird, only that short molting period (Smithsonian Institution, 1976). Place and time of molting must be known as well as species, age, sex, and food of the birds whose feathers are studied. Also standardized sample preparation is needed since washing technique and the portion of the feather used for analysis cause variations in results (Hanson and Jones, 1976).

Several Swedish investigators have determined mercury in feathers. Berg et al. (1966) looked at feathers from skins and mounted specimens dating back to 1840 as well as feathers from living and freshly killed birds. They found by neutron activation analysis "roughly constant Hg levels in each species studied between 1840 and 1940." They also found a distinct increase of mercury in the feathers, dating in the 1940's and the 1950's, when alkyl mercury was widely used as a seed dressing. This increase, as much as 10 to 20 times, was found in seed-eating birds and their predators. Westermark et al. (1975) confirmed Berg's findings and also reported a distinct decrease in mercury in the feathers after 1966 when the use of alkyl mercury as a seed dressing was prohibited in Sweden.

Hanson and Jones (1976) analyzed feathers of Blue, Snow and Ross' geese for twelve minerals during a study to determine whether feather mineral patterns could be used to ascertain geographic origins. The minerals measured were Ca, Mg, Na, K, P, Fe, Zn, Mn, Cu, B, Si, and Al. The suppositions were that: 1) feather mineral patterns reflected the mineral content of the food materials, mainly plants, and 2) the food plants in turn reflected the mineral pattern of the soils, the underlying rocks and the sediments carried into the area by water and wind. They concluded that "the levels of macroelements in the primary feathers must be related first to the total complex of environmental minerals and secondarily to the metabolic regulation of absorption of elements individually." The metals Fe, Mn, Cu, Si, B, and Al appeared to be more directly related to environmental levels and less subject to metabolic regulation of absorption than the other elements studied. Differences within a colony were due to variables such as sex, age, stage of feather growth, and portion of the feather used for analysis.

Use of feathers for retrospective monitoring of heavy metals appears to offer promise. A good sized repository of museum skins is available but the usefulness of these specimens depends on their treatment after collection and on availability of adequate numbers from geographic areas of interest. Additional studies on mineral deposition in feathers are needed.

Food plants, when they can be used, would seem to be more direct indicators of heavy metal levels than feathers, hair, nails, horns, etc. whose mineral content is derived from these plants.

Hair

Metal concentrations of Cd, Pb, Ni, Co, Si, Mn, Al, Cr, Ag, Cu, Fe, etc. in human hair have been determined through numerous studies. Hair has a tendency to accumulate metals because hair is rich in cysteine, a sulfhydryl containing amino acid, which complexes with many heavy metals. Human hair also has many of the characteristics of an ideal tissue for epidemiologic

study. Hair is painlessly removed, normally discarded, easily collected, and metabolically passive after emerging from the scalp.

Gross, Yeager, and Middendorf (1976) studied cadmium concentrations in hair, liver, and kidney tissue obtained during autopsy examinations of residents from the Cincinnati area. As shown in Table 15, there was an increase of cadmium concentration in the liver until the late decades. In the kidney, there was an increase of cadmium concentration to the fourth decade and a steady decrease from the sixth decade. The high cadmium concentration in the hair occurred during early infancy and decreased with age.

TABLE 15. AGE GROUP MEANS AND STANDARD DEVIATIONS FOR TISSUE CADMIUM

	Liver			Kidney			Hair		
Age Group	N	$\bar{X}$	± SD	N	$\bar{X}$	± SD	N	$\bar{X}$	± SD
Abortuses	19	0.01	0.00	19	0.07	0.06	1	0.20	
0-1 months	7	0.01	0.01	7	0.05	0.04	4	0.45	0.35
1-23 months	9	0.05	0.05	9	0.13	0.09	5	3.30	1.29
2-5 years	7	0.33	0.35	7	13.33	22.72	7	2.17	0.84
6-12 years	4	0.66	0.49	4	6.23	6.71	4	1.52	1.01
13-18 years	11	0.97	0.69	11	8.57	3.97	11	1.48	1.14
19-24 years	10	0.82	0.54	10	13.73	6.99	10	1.49	2.10
25-34 years	10	1.25	0.75	10	24.40	14.10	9	0.67	0.56
35-44 years	6	0.88	0.66	6	29.62	14.97	6	2.19	2.09
45-54 years	3	1.75	1.86	2	39.35	13.79	3	0.66	0.20
55-64 years	9	1.96	1.30	9	30.09	17.22	8	0.57	0.44
65+ years	10	1.97	1.08	10	20.89	12.26	10	0.81	0.67
Total	105	0.88	1.19	104	13.65	17.60	78	1.48	1.58

Hammer et al. (1971) analyzed the hair of school children from five different cities. Their data along with exposure rankings are given in Table 16. They found mean hair metal levels for As, Cd, and Pb accurately reflected community exposure (Table 17).

Adler, Samuel, and West (1977) studied the anatomical and longitudinal variation of trace metal concentrations in human hair. They found no systematic difference in the average trace metal concentrations in hair from different anatomical sites, i.e., scalp, arm, leg, and axilla. In many cases the trace metal content was generally higher at the distal end than at the root.

Chattopadhyay, Roberts, and Jervis (1977) studied the correlation of lead concentrations in hair and blood of children residing near smelters. They

TABLE 16. EXPOSURE RANKINGS FOR FIVE SELECTED METALS IN FIVE SELECTED CITIES*

City	Major Industries	Metal Exposure Rankings				
		Arsenic	Cadmium	Copper	Lead	Zinc
I	Lead and zinc mining and smelting	Intermediate	High	Intermediate	Highest	Intermediate
II	Lead and zinc smelting	High	High	Low	High	Intermediate
III	Copper smelting	Highest	Low	Intermediate	Low	Low
IV	Government and commercial†	Intermediate	Low	Low	Low	Low
V	Education and farm trading	Low	Low	Low	Low	Low

*Exposure ranking determined from acrometric, geologic, and industrial data with "low" ≤ ordinary United States urban exposures.
†Located near the lead and zinc smelting city.

observed that persons exposed to massive and irregular doses of lead may not exhibit elevated lead levels in blood but will invariably show high lead concentrations in hair. The lead concentrations in children living close to a smelter and concentrations in a control child living in an urban area are shown in Table 18.

Kopito and Shwachman (1975) investigated the effects of age, sex, and geographical location on the lead concentration in hair. The place of residence appeared to be a major determinant of the initial amount of lead in hair and its accumulation with time. In explaining the lead concentration difference between the proximal and distal segments they assumed that a fraction of the lead in the hair close to the scalp is of endogenous origin and that the additional accumulation of lead in the more distal segments is, most likely, due to exogenous lead. They indicted no age or sex-related differences in the accumulation of lead in hair.

The trace metal concentrations in human hair are a function of many factors such as age, sex, hair length, personal chemical treatment, geographical location of residence, etc. The difficulties that exist in obtaining a complete history of hair, the lack of differentiation between exogenous and endogenous metal concentration, and the limited information on turnover rates of metals in hair exclude it as a tissue for retrospective monitoring.

Nails

Fingernails have been analyzed for trace metals mostly in attempts to discover changes in metal metabolism in certain pathologic conditions such as kidney failure and cystic fibrosis (Mahler, 1970). Mn, Na, Cu, Au, and Zn were determined in hair and fingernails by neutron activation analysis.

TABLE 17. DESCRIPTIVE SUMMARIES FOR HAIR TRACE METAL LEVELS; DISTRIBUTION BY METAL AND CITY

Metal	Exposure Ranking	Descriptive Summary: Geometric Mean (ppm)	Median (ppm)	Arithmetic Mean (ppm)	Standard Deviation (ppm)	Sample Size
Arsenic	Highest (III)	9.1	9.1	10.6	7.00	31
	High (II)	3.0	4.0	5.2	6.00	16
	Intermediate (I)	1.2	1.1	1.7	1.48	32
	Intermediate (IV)	0.7	0.7	0.8	0.33	13
	Low (V)	0.3	0.4	0.4	0.26	28
Cadmium	High (I)	2.1	2.1	3.5	4.94	45
	High (II)	1.5	1.6	2.0	1.54	25
	Low (III)	1.0	1.0	1.3	0.99	37
	Low (IV)	1.0	0.9	1.3	1.30	21
	Low (V)	0.7	0.8	0.9	0.58	37
Copper	Intermediate (I)	17.1	13.0	25.7	28.1	45
	Intermediate (III)	13.9	12.0	15.3	7.5	37
	Low (II)	10.4	11.0	11.8	3.0	25
	Low (IV)	11.5	11.0	12.6	6.0	21
	Low (V)	14.4	11.0	22.5	34.7	37
Lead	Highest (I)	57.7	52.0	107.1	131.8	45
	High (II)	22.8	20.0	44.3	49.3	25
	Low (III)	10.5	13.0	24.3	14.1	37
	Low (IV)	8.9	7.9	12.1	11.4	21
	Low (V)	6.1	6.5	7.6	5.0	38
Zinc	Intermediate (I)	149.6	160.0	154.0	33.7	45
	Intermediate (II)	141.9	145.0	145.2	30.8	25
	Low (III)	154.3	160.0	156.6	26.0	37
	Low (IV)	149.9	160.0	155.4	36.9	21
	Low (V)	149.9	155.0	154.2	32.5	38

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TABLE 18. LEAD CONTENT OF SEGMENTS OF STRANDS OF HAIR

Sample Description	Hair Lead Content, ppm				
	Case #3	Case #4	Case #5	Case #6	(Control) Case #7
0 - 2 cm	126	100	44	202	30
2 - 4 cm	95	161	79	146	26
4 - 6 cm	108	216	89	138	24
6 - 8 cm	132	105	58	100	20
8 - 10 cm	105	65	60	124	18
10 - 12 cm	104	244	94	---	21
12 - 14 cm	115	156	110	---	19
14 - 16 cm	88	76	---	---	25
16 - 18 cm	78	282	---	---	26
18 - 20 cm	100	---	---	---	23
20 - 22 cm	101	---	---	---	20
22 - 24 cm	183	---	---	---	18
24 - 26 cm	227	---	---	---	20
Weighted average	120	147	72	121	25
Whole hair	122	137	79	129	27

Mahler found a very large difference in trace metal content of both hair and nails which seemed to be related to geographic origin rather than disease conditions. Mercury analyses of thumbnails of dentists and dental workers (Kanabrocki, 1977) showed definitely higher levels than in a control group and accumulation was time dependent.

Although the nails do demonstrate accumulation of some metals, feasibility of this tissue for retrospective monitoring appears to be slight due to lack of adequate numbers of samples, to problems in dating and in knowing whether the material measured was adsorbed on the surface or absorbed via metabolic routes. The other keratinized materials (hair and feathers) do reflect environmental levels of metals, however, the effects of many variables remain to be determined.

REPOSITORY SAMPLES

Herbarium specimens are good candidates for indicators of past pollutants particularly because the specimens are dated, the site of their collection pinpointed, and their treatment following collection exposes them to a minimum of contamination. Specimens are kept separated during field collection. The only possible sources of chemical contamination in the field are from the newsprint into which the plant specimens are inserted or the corrugated

cardboard separators used between the pockets of newsprint. Once collected, specimens are dried with gentle heat between fresh layers of newsprint (or in some cases old newspapers) with paper felts and corrugated cardboard ventilators between the specimens. When dried the specimens are mounted generally on rag paper with a neutral opaque library paste. This paste is often diluted with water which would be another possible source of contamination. Specimens are often fixed in place with gummed linen tape plus a reinforced ethyl cellulose plastic stripping. Specimens are stored in closed cases and protected against insect damage either by periodic fumigation, usually with methyl bromide, or more often by the presence of naphthalene or p-diclorobenzene (Savile, 1962).

A survey of herbarium problems was published in 1978 and covered the techniques used in the 70 largest herbariums in the United States. These techniques were similar to those outlined above. The survey indicated the variety of adhesives and insecticides used by the various herbariums. As to retrospective monitoring, it seems likely that treatment of specimens and any resultant contaminants could be discovered from the procedural records kept by the herbariums, thus minimizing the problem of interfering pollutants.

It is a matter of chance that enough specimens will have been collected from one location over a time period. However, based on the existence of records of date, source, and treatment and the dry storage plus numbers of specimens, herbarium specimens appear to be one of the most potentially valuable retrospective pollution monitors. Pollutants which could be studied are those deposited or adsorbed onto the surfaces of the plant material or those which cause specific morphological changes.

There are very few reports in the literature of actual studies of herbarium specimens as retrospective pollutant monitors. Hajduk (1972) found morphological abnormalities in recently collected plant materials compared to those from an herbarium. He also found increases in the numbers of mineral and soot particles found on recently collected specimens as compared with those collected about 1913 at Pezinok near Bratislava. The types of necrotic changes observed in recent specimens could be reproduced by exposing growing plants to various air pollutants.

Rühling and Tyler (1968) made an historical study of lead concentrations from 1860 to 1968 by using 3 species of mosses which had been preserved in the Botanical Museum of Lund. They found two periods of increase from 1875 to 1900 and from 1950 to 1968. Base values of about 20 ppm were found in the years 1860-1875 and increased to values of about 80-90 ppm in 1968. All samples were collected in Skane. Analysis of moss from the sparsely populated northern part of Scandinavia showed very low levels of lead.

Johnsen and Rasmussen (1977) and Rasmussen (1977) also used herbarium specimens of epiphytic bryophytes for retrospective studies of heavy metals. The former study used the species Pterogonium gracile (Hedw.) Sm. which was collected from the same phorophyte ten times from 1944-1976. Significant increases in Pb, V, and Zn were observed and increased trends were also found for Cu, Cr, and Ni. The sequence of metal concentrations in the moss was found to correspond well with the sequence found for bulk precipitation.

Rasmussen analyzed for thirteen metals in five species of moss collected from numbered trees in 1951, 1973, and 1975. The amounts of Cr, Cu, Fe, Ni, Pb, V, and Zn increased 42-108 percent from 1951-1975. Lack of duplicated specimens from identical sampling sites in different years and lack of exact data related to sampling site and substrate were indicated as possible difficulties in using herbarium specimens by Johnsen and Rasmussen (1977). If there are enough specimens which ovecome these difficulties, herbarium collections, particularly of epiphytic bryophytes, are promising for retrospective monitoring.

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